

PATENT APPLICATION

TITLE: A SYNTHETIC LUBRICANT BASESTOCK AND AN INTEGRATED FISCHER-TROPSCH PROCESS FOR ITS PRODUCTION

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A SYNTHETIC LUBRICANT BASESTOCK AND AN
INTEGRATED FISCHER-TROPSCH PROCESS FOR ITS PRODUCTION

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CROSS REFERENCE TO RELATED APPLICATIONS

[1] Not applicable.

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FEDERALLY SPONSORED RESEARCH

[2] Not applicable.

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REFERENCE TO MICROFICHE APPENDIX

[3] Not applicable.

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FIELD OF THE INVENTION

[4] The invention relates to a synthetic lubricant basestock and more particularly, to a lubricant basestock produced from an integrated Fischer-Tropsch synthesis and which provides both thermal and oxidative stability and good cold flow properties. The invention further relates to the integrated Fischer-Tropsch process for producing the synthetic lubricant basestock.

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BACKGROUND OF THE INVENTION

[5] Lubricant basestocks made from Fischer-Tropsch waxes are fundamentally different from lubricant basestocks available from any other source, including basestocks made from petroleum or mineral waxes, mineral wax hydrocracker and pipe still bottoms and those oligomerized from lower molecular weight petrochemicals or petroleum cuts. The first difference is the composition of the Fischer-Tropsch wax as compared to the compositions of other high molecular weight components of petroleum. Fischer-Tropsch waxes are, as a result of specific catalytic synthesis, composed of linear paraffins, a small amount of predominantly terminal methyl-branched paraffins, and a small amount of linear olefins. In addition to linear paraffins, petroleum-derived waxes contain large amounts of branched paraffins with varying

branch-chain lengths, as well as substituted naphthenes, polynaphthenes, substituted aromatics and polyaromatics.

[6] The second difference arises from the common hydroprocessing methods applied to Fischer-Tropsch and mineral waxes to convert them into lubricant basestocks. Such hydroprocessing normally employs acidic dual function hydroisomerization and hydrodewaxing catalysts which: a) isomerize normal chains into methyl-branched chains; b) crack heavier paraffins into lighter paraffins; and c) saturate any phenyl or olefinic unsaturation. When applied to highly linear Fischer-Tropsch product the hydroprocessing catalyst introduces predominantly multiple methyl branching along the carbon backbone.

When applied to the linear paraffin components of a mineral wax, the catalyst will generate methyl branches in exactly the same manner. However, acting on the branched paraffin components which are present in large quantities in mineral waxes, acidic dual function catalysts results in complex and extensive branching.

[7] Furthermore, acidic dual function catalysts catalyze a number of reactions with benzylic and naphthenic compounds present in mineral waxes. Such reactions include, for example: (1) hydrogenation of phenyl compounds to naphthenics; (2) addition of methyl-branching to an alkyl group or to a ring of a naphthene; and (3) cleaving of naphthenic rings to long-chain branched isoparaffinic compounds. Thus, application of the same hydroprocessing technology to Fischer-Tropsch waxes and to mineral waxes generate product mixtures which have structurally dissimilar components.

[8] It is well known that desirable lubricant basestock characteristic such as low pour point are enhanced by the presence of non-linear isomers, while other desirable characteristics such as thermal and oxidative stability are worsened by the same isomers. Polyalphaolefins synthesized from specific alpha-olefins, useful as synthetic lubricant basestocks, have a proper balance between long-chain branching and linearity, resulting in a balance between low temperature properties and thermal and oxidative stability. In contrast, the only way to influence these properties in hydroprocessed Fischer-Tropsch waxes, is to control the number of methyl branches along the straight chain which in contrast to long-chain branching has a more pronounced adverse effect on the stability of a resulting baseoil. Polyalphaolefins, however, are significantly more expensive to produce than Fischer-Tropsch derived lubricant basestocks.

[9] Although Fischer-Tropsch based lubricant basestocks and processes for their manufacture are known in the art, such processes generally utilize only the wax, and not the oil, portion of the Fischer-Tropsch product. Therefore, such Fischer-Tropsch processes inherently have low yields because the necessary step of wax isomerization is accompanied by cracking, resulting in only 30% to 50% conversion of the wax Fischer-Tropsch product into lubricant basestock. Moreover, the wax feed constitutes only from about 30% to about 70% of the total Fischer-Tropsch product.

[10] Lubricant basestocks are typically fractionated into final products having varying viscosities, with one of the typical lubricant basestock product slates including fractions having viscosities of: (1) 2 centistokes (cSt); (2) 3 cSt; (3) 5 cSt; and (4) 7 cSt. Fischer-Tropsch based synthetic lubricant basestocks, however, are heavily skewed to low viscosity components. Specifically, Fischer-Tropsch wax ("HFTL") contains a declining amount of heavier hydrocarbons in accordance with the Schultz-Flory distribution. Such distribution, in conjunction with the effects of hydroprocessing, each step of which results in at least some hydrocracking, ensure that conventionally produced Fischer-Tropsch derived lubricant basestock have a significantly greater portion of lower viscosity components: typically, there is a greater amount of 3 cSt product than 5 cSt product and a greater amount of 5 cSt product than 7 cSt product. In contrast to the viscosity profile of the synthetic lubricant basestock, the market demand is weighted toward the middle viscosity components, those with viscosities between about 4 cSt and 6 cSt.

[11] Oligomerization of the lighter Fischer-Tropsch products to yield hydrocarbons of sufficient carbon number for use in a lubricant basestock has not heretofore been considered because of the presence of oxygenates, which are active in systems with oligomerization catalysts. In some oligomerization systems, oxygenates are a needed co-catalyst in suitable catalytic amounts. However, in large concentrations oxygenates retard oligomerization or act as catalyst deactivation agents. Moreover, lighter Fischer-Tropsch products generally have low olefin concentration and would therefore, yield little oligomerization product. Finally, the olefin content which is present in lighter Fischer-Tropsch product streams generally have a relatively low ratio of alpha-olefins to internal-olefins, further complicating oligomerization and decreasing oligomerization yield.

[12] Therefore, a need exists for a high yield, economical process to produce a synthetic lubricant basestock. There is a further need for a synthetic lubricant basestock which incorporates at least some long-chain branching and has both good low temperature properties, such as pour point, and good thermal and oxidative stability. There is yet an additional need
5 for a process to produce a synthetic lubricant basestock which contains proportionately more middle or high viscosity product.

SUMMARY OF THE INVENTION

10 [13] An integrated Fischer-Tropsch process comprising (or alternatively consisting or consisting essentially of) the steps of producing a synthetic crude by a Fischer-Tropsch reaction of synthesis gas, fractionating the synthetic crude at least into a light Fischer-Tropsch liquid and a heavy Fischer-Tropsch liquid, optionally dehydrating alcohols in the light Fischer-Tropsch liquid into corresponding alpha- and internal-olefins, oligomerizing the light Fischer-Tropsch liquid to form a heavy branched olefin stream, hydroprocessing the heavy Fischer-Tropsch liquid to form a crude baseoil, and introducing the heavy branched olefin stream and
15 crude baseoil into a hydrofinisher to produce a synthetic lubricant basestock.

[14] A baseoil composition produced by an integrated Fischer-Tropsch process comprising at least 40% of methyl branched hydrocarbons, characterized by BI of 24% and above and DM
20 of 18% and above and at least 5% long-chain branched wherein the branches have a carbon number of at least 2, characterized by BI of 24% and below and DM of 21% and below.

[15] A baseoil composition produced by an integrated Fischer-Tropsch process comprising at least 40% of methyl branched hydrocarbons with a pour point of at most -10°C, and at least 5% long chain branched hydrocarbons having a pour point equal to or less than -30°C.
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BRIEF DESCRIPTION OF THE DRAWINGS

[16] Fig. 1 is an illustration of the branching index and distant methylene percentage for theoretical compounds designated "A" and "B" wherein compound A is a C₃₀ molecule having
30 a single 3 carbon side-chain on the tenth carbon of the backbone and compound B is a C₃₀ molecule with a single methyl side-chain located on each of the second, tenth, and twentieth carbons.

[17] Fig. 2 is a schematic diagram of the front end of the integrated Fischer-Tropsch process of the invention.

[18] Fig. 3 is a schematic of the dehydration process of the integrated Fischer-Tropsch process.

5 [19] Figs. 4A-4D are schematic diagrams of alternative hydroprocessing schemes useful in the process of the invention.

[20] Fig. 5 is a schematic diagram of the post-dehydration processing of the process of the invention.

10 [21] Fig. 6 is a chart comparing viscosity profiles of a hypothetical synthetic lubricant basestock produced in accordance with the invention and a synthetic lubricant basestock produced by Fischer-Tropsch processes of the prior art.

DESCRIPTION OF EMBODIMENTS OF THE INVENTION

15 [22] The term C_x , where x and y are numbers greater than zero, refers to hydrocarbon compound having predominantly a carbon number of x . As used herein, the term C_x may be modified by reference to a species of hydrocarbons, such as, for example, C_5 olefins. In such instance, the term means an olefin comprised predominantly of pentene but which may have impurity amounts of olefins of other carbon numbers such as hexene, heptene, propene, or
20 butene. The term C_x-C_y , where x and y are numbers greater than zero, refers to a mixture of hydrocarbon compounds wherein the predominant component hydrocarbons have carbon numbers between x and y . For example, the term C_5-C_9 hydrocarbons means a mixture of hydrocarbon compounds which is predominantly comprised of hydrocarbons having carbon numbers between 5 and 9 but may also include impurity level quantities of hydrocarbons
25 having other carbon numbers.

[23] The term "branching index" ("BI") means the percentage of methyl hydrogens. The term "DM" means the percentage of methylene carbons which are the fourth or greater carbon from an end group or branch carbon. Such methylene carbons are called "distant methylene carbons." For illustration, a C_{30} molecule incorporating a single three carbon side-chain on the
30 tenth carbon on the backbone, compound A, is shown in Fig. 1. The methylene carbons which are the fourth or greater carbon from an end group or branch carbon are circled. The structure illustrated in Fig. 1 would have three methyl groups, nine hydrogens on methyl groups, a total

of sixty-two hydrogens, a BI of 14.5%, and 12 distant methylene carbons, 30 total carbons, and a DM of 40%. In contrast, a C₃₀ molecule with a single methyl group at each of the C₂, C₁₀ and C₂₀ backbone carbons, compound B, will have five methyl groups, fifteen hydrogens on methyl carbons, a total of sixty-two hydrogens, a BI of 24.2%, 4 distant methylene carbons, 30 total carbons, and a DM of 13.3%. Again, the distant methylene carbons are circled in the illustration of compound B in Fig. 1.

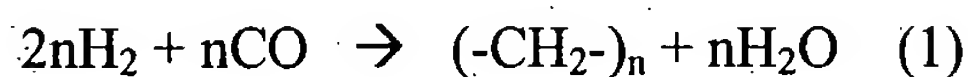
[24] Practically, in the absence of knowledge of the exact structure of a lubricant basestock molecule, BI and DM can be measured by C¹³ NMR, using for example, the method described in U.S. 6,008,164, which is herein incorporated by reference. In the carbon backbone of an isoparaffin, a methyl carbon has a unique chemical shift. Carbons that are part of methylene groups located first, second and third from the methyl group are influenced by the methyl carbon. Their chemical shifts are distinct from each other and from those methylene groups that are fourth and more from the methyl group. Similarly, the CH group, that anchors a branch to the backbone, has a specific signature. And in the same manner, carbons that are located first, second and third from the tertiary carbon are influenced by the tertiary carbon and thus have unique chemical shifts. In contrast, those carbons that are fourth and further removed from the tertiary carbon from all have essentially the same shift. Thus, both BI and DM are measures of the amount and type of branching of an isoparaffin molecule. As it is evident from the simplistic example in Fig. 1, a long chain-branched isoparaffin would have fewer methyl branches and longer spans of linear chains, resulting in lower BI and higher DM. This tendency is evidenced, for example, by empirical measurements contained in U.S. 6,090,989, the disclosure of which is herein incorporated by reference.

[25] The integrated Fischer-Tropsch process includes processing of synthesis gas to produce a hydrocarbon stream via the Fischer-Tropsch reaction, recovery of the Fischer-Tropsch product, catalytic dehydration of all or part of the Fischer-Tropsch product, recovery of the hydrocarbons, oligomerization of a light Fischer-Tropsch liquid, hydroprocessing of a heavy Fischer-Tropsch, and final processing of the light and heavy fractions into a lubricant basestock. A wide variety of Fischer-Tropsch reaction processes are known in which reaction conditions, catalysts, and reactor configurations vary. The integrated Fischer-Tropsch process of the invention may be used with any such reaction conditions, catalysts, and reactor configurations. For the purposes of the description below, one known Fischer-Tropsch

synthesis is described. Other variations of Fischer-Tropsch synthesis are described, *inter alia*, in U.S. 4,973,453; 6,172,124; 6,169,120; and 6,130,259; the disclosures of which are all incorporated herein by reference.

[26] Three basic techniques may be employed for producing a synthesis gas, or syngas, which is used as the starting material of a Fischer-Tropsch reaction. These include oxidation, reforming and autothermal reforming. As an example, a Fischer-Tropsch conversion system for converting hydrocarbon gases to liquid or solid hydrocarbon products using autothermal reforming includes a synthesis gas unit, which includes a synthesis gas reactor in the form of an autothermal reforming reactor ("ATR") containing a reforming catalyst, such as a nickel-containing catalyst. A stream of light hydrocarbons to be converted, which may include natural gas, is introduced into the reactor along with oxygen (O₂). The oxygen may be provided from compressed air or other compressed oxygen-containing gas, or may be a pure oxygen stream. The ATR reaction may be adiabatic, with no heat being added or removed from the reactor other than from the feeds and the heat of reaction. The reaction is carried out under substoichiometric conditions whereby the oxygen/steam/gas mixture is converted to syngas.

[27] The Fischer-Tropsch reaction for converting syngas, which is composed primarily of carbon monoxide (CO) and hydrogen gas (H₂), may be characterized by the following general reaction:



Non-reactive components, such as nitrogen, may also be included or mixed with the syngas. This may occur in those instances where air, enriched air, or some other non-pure oxygen source is used during the syngas formation.

[28] The syngas is delivered to a synthesis unit, which includes a Fischer-Tropsch reactor ("FTR") containing a Fischer-Tropsch catalyst. Numerous Fischer-Tropsch catalysts may be used in carrying out the reaction. These include cobalt, iron, ruthenium as well as other Group VIIIIB transition metals or combinations of such metals, to prepare both saturated and unsaturated hydrocarbons. The Fischer-Tropsch catalyst may include a support, such as a metal-oxide support, including silica, alumina, silica-alumina or titanium oxides. For example, a cobalt (Co) catalyst on transition alumina with a surface area of approximately 100-200 m²/g may be used in the form of spheres of 50-150 μm in diameter. The Co concentration on the support may also be 5 to 30wt%. Certain catalyst promoters and stabilizers may be used. The

stabilizers include Group IIA or Group IIIB metals, while the promoters may include elements from Group VIII or Group VIIB. The Fischer-Tropsch catalyst and reaction conditions may be selected to be optimal for desired reaction products, such as for hydrocarbons of certain chain lengths or number of carbon atoms. Any of the following reactor configurations may be employed for Fischer-Tropsch synthesis: fixed bed, slurry bed reactor, ebullating bed, fluidizing bed, or continuously stirred tank reactor ("CSTR"). The FTR may be operated at a pressure from about 100 to about 800 psia and a temperature from about 300° F to about 600° F. The reactor gas hourly space velocity ("GHSV") may be from about 1000 to about 15000 hr⁻¹. Syngas useful in producing a Fischer-Tropsch product useful in the invention may contain gaseous hydrocarbons, hydrogen, carbon monoxide and nitrogen with H₂/CO ratios from about 1.5 to about 3.0. The hydrocarbon products derived from the Fischer-Tropsch reaction may range from methane to high molecular weight paraffinic waxes containing more than 100 carbon atoms.

[29] Referring to Fig. 2, a front end portion of the integrated Fischer-Tropsch process is illustrated. Synthesis gas produced in an autothermal reactor 10 passes through conduit 1 into a Fischer-Tropsch reactor 2. The tail gas of the Fischer-Tropsch product is recovered overhead through conduit 3 and the Fischer-Tropsch oil and wax are fractionated and recovered through conduits 4 and 5, respectively. The product recovered in conduit 4 is referred to as a Light Fischer-Tropsch Liquid ("LFTL"), and the product recovered in conduit 5 is referred to as a Heavy Fischer-Tropsch Liquid ("HFTL"). Alternatively, the LFTL and HFTL may be further fractionated into at least a nominally 30° to 550°F distillate and 500°F+ bottoms stream. The LFTL and HFTL may also be fractionated into a number of other fractions as may be required by the product slate.

[30] All or part of the LFTL, which is comprised primarily of C₄ to C₂₂ paraffins, is fed into the dehydration unit 6. In the integrated Fischer-Tropsch process, primary and internal alcohols present in the LFTL are dehydrated to yield corresponding olefins, according to the following reaction:



[31] Referring now to Fig. 3, a schematic of the dehydration unit of the integrated Fischer-Tropsch process is shown. The LFTL stream is vaporized in a preheater 20. The vaporized LFTL stream at a temperature from about 400°F to about 800°F is passed through line 21 into

one or more packed beds within unit 22 where it is contacted with a dehydration catalyst, such as activated treated alumina or silica-alumina. Essentially all of the primary and internal alcohols present in the vaporized LFTL are dehydrated to their corresponding olefins, with conversion rates of at least 95%.

5 [32] Dehydration reaction temperature may range from between about 500° and 700°F. The vaporized feed for the dehydration unit may be superheated prior to being fed into packed beds 22 or alternatively, may be heated within packed beds 22. The LHSV of packed beds 22 may range from about 0.10 hr⁻¹ to about 3.0 hr⁻¹. Reaction pressure may be maintained by the pressure of the accumulator and must be such to vaporize all of the dehydration feed.
10 Typically, the pressure may range from between about 0 psia and about 100 psig. The LFTL stream may be mixed with nitrogen gas or steam prior to or after preheater 20. The nitrogen gas or steam acts to help vaporizing heavier components of the LFTL stream.

[33] In an alternative embodiment, a moving bed of alumina or silica-alumina catalyst may be used. Coking is an undesirable side reaction in this synthesis. Fluidized beds, slurry beds or
15 ebullating beds may be used with continuous batch or semi-batch catalyst removal and regeneration. The catalyst may be removed by one of these methods and regenerated by passing a mixture of nitrogen and oxygen or air at elevated temperatures over the catalyst.

[34] Depending upon the alumina used, some of the olefins present or produced in packed beds 22 may also be isomerized to internal olefins. Alumina catalysts useful for the
20 dehydration of alcohols are known and include, for example, gamma-alumina, pacified alumina, and activated alumina. Commercially available alumina useful in the integrated Fischer-Tropsch process include, for example, S-400 and DD-470 alumina catalysts made and sold by Alcoa. Alumina catalysts for use in the integrated Fischer-Tropsch process generally contain at least about 90wt% Al₂O₃, oxides of silicon and iron present in amounts of less than
25 about 0.1wt%, and oxides of sodium present in an amount of less than about 1 wt%. The alumina catalysts are generally supplied as substantially spherical particles having diameter from about one-sixteenth to about one-half inch.

[35] In an alternative embodiment, all or part of the HFTL may also be dehydrated. In such cases, the operating pressure of the accumulator, and thus the packed beds, should be adjusted
30 to vaporize the HFTL stream.

[36] Referring still to Fig. 3, the dehydrated product is recovered through line 24 into condenser 25, where it is condensed. The condensed product will contain aqueous and organic phases which may be separated in an accumulator 26. Both the organic and aqueous phases are essentially free of alcohols, the alcohols having been essentially completely dehydrated. The organic phase primarily contains paraffins with some olefins, the olefins arising from dehydration of the alcohols as well as from the Fischer-Tropsch product.

[37] In the inventive process, the HFTL may be hydrocracked and hydrotreated in a number of possible sequences. Figures 4A-4D illustrate a number of possible hydroprocessing combinations. For example, as shown in Fig. 4A, the HFTL may be first hydrotreated in hydrotreater 30 and subsequently hydrocracked in hydrocracker 31. Alternatively, the HFTL may be hydrocracked in hydrocracker 32 and subsequently hydrotreated in hydrotreater 33 as shown in Fig. 4B. In each of the hydroprocessing schemes of Figs. 4A and 4B, the hydroprocessed HFTL is sent to a fractionator 34, or hydrocracked, fractionated and the heavy recycle may be hydrotreated. Hydrocracking and hydrotreating conditions and parameter ranges are known to those of ordinary skill in the art. Examples of hydroprocessing conditions and parameters are described in U.S. Patents 6,274,029; 6,296,757; 6,180,842; and Australian Patent No AU-B-44676/93, the disclosures of which are incorporated herein by reference. Other conditions and parameters which are well known to those in the art are also useful in the invention.

[38] All or part of the hydrocracker fractionator bottoms are routed to a hydrodewaxer 56 as shown in Fig. 5. Hydrodewaxing conditions are well known to those skilled in the art and may include, for example, a GHSV of from about 0.2 hr^{-1} to about 2.0 hr^{-1} , a hydrogen partial pressure between about 200 and about 2000 psig, a catalyst average temperature of between about 400° and about 750°F , and a recycle gas ratio between about 1,000 and about 10,000 SCF/bbl on a hydrogen basis. The reaction is generally conducted over a shape-selective catalyst substrate impregnated with a noble metal. Acceptable substrates include, for example, silico alumino phosphate ("SAPO") and zeolitic molecular sieves, such as that commonly known as ZSM-5. Hydrodewaxing is further described, *inter alia*, in US6506297, 5882505, 5976351, 6008164, the disclosures of which are incorporated herein by reference. Hydrodewaxing is carried out to make a product having a pour point between about 0° and

about -30°C . The hydrodewaxed product is then fractionated to isolate the desired lubricant basestock fraction, which is then sent to a hydrofinisher 57.

[39] Figs. 4C and 4D show other hydroprocessing schemes which may be used in the present invention. Fig. 4C illustrates a process in which all or part of the HFTL is first hydrocracked in hydrocracker 35, followed by fractionation in fractionator 35, followed by fractionation 38 and finally hydrotreatment in hydrotreater 36. A bottoms, heavier portion, of the hydrotreater product may be recycled to hydrocracker 35. Alternatively, as shown in Fig. 4D, all or part of the HFTL may be only hydrocracked in hydrocracker 37, followed by fractionation in separator 39. In the embodiment illustrated by Fig. 4D, the heavy fraction from the separator 39 is not recycled.

[40] Referring now to Fig. 5, the product of dehydration, which may be the entire LFTL or a portion of it, enters separator 50 through conduit 49 and is fractionated in separator 50 to produce a nominal $\text{C}_9\text{-C}_{18}$ fraction, a 300° to 600°F cut. This fraction, containing between about 5 and about 30wt% olefin is then fed through conduit 52 into an oligomerization reactor 51 containing a BF_3 /co-catalyst system. The oligomerization reactor 51 may be a plug flow reactor, a loop reactor, or two to five CSTRs in series. The co-catalyst used with BF_3 is an oxygen-containing compound such as, for example methanol, ethanol, propanol, butanol, other mono-alcohols, glycol ethers, and polyglycol ethers. The BF_3 /co-catalyst system may be preformed, or formed in-situ via addition of gaseous BF_3 to the mixture of oxygen-containing compound alcohol and hydrocarbons. The reaction temperature may range from 50° to 200°F . The amount of catalyst added to the hydrocarbon mixture may range from about 1 to about 15 parts of BF_3 and from about 1 to about 20 parts of a co-catalyst per 100 parts of reactants. Other common catalyst systems may also be used for oligomerization, such as AlCl_3 /co-catalyst, solid phosphoric acid catalysts, and solid acidic resins. Alternative olefin oligomerization methods which may be used in the inventive process are known in the art. For example, U.S. Patent 6,525,149, the disclosure of which is incorporated herein in its entirety by reference, discloses a polyolefin preparation process utilizing a stable complex of BF_3 and a complexing agent therefor.

[41] Alternatively, $\text{C}_9\text{-C}_{13}$ (nominally 300° to 450°F) and $\text{C}_{14}\text{-C}_{18}$ (nominally 450° to 600°F) fractions may be isolated and oligomerized separately to produce a narrower distribution of oligomers. The $\text{C}_9\text{-C}_{13}$ fraction must be trimerized or tetramerized to reach a useful baseoil

range, while the C₁₄-C₁₈ fraction only needs to be dimerized to reach a baseoil range. Furthermore, the C₁₄-C₁₈ fraction may be isomerized to randomize the position of the double bond and subsequently oligomerized. While olefins in the C₉-C₁₃ fraction are approximately two-thirds alpha-olefins and one-third internal olefins by weight, with 2- cis and trans internal olefins predominating, only about one-half of the olefins in the C₁₄-C₁₈ fraction are alpha-olefins. In one embodiment of the invention, the alpha-olefins, in both or either of the C₉-C₁₃ and C₁₄-C₁₈ fractions, are isomerized to internal olefins prior to oligomerization by passing the desired fraction from separator 50 through conduit 53 into isomerizer 54. The isomerized olefins are then passed through conduit 55 into oligomerization reactor 51. Isomerization may be accomplished by passing the stream over high-surface alumina impregnated with potassium or sodium. Alternative isomerization catalysts useful in the invention include zeolites and/or SAPO substrates impregnated with one or more noble metals. Other isomerization catalysts which may be used include iron pentacarbonyl, solid acidic resins and derivatives thereof. The reaction is conducted in the liquid phase at a temperature between about 200° to about 600°F. Olefin isomerization methods and conditions are known, including those disclosed in U.S. Patents 5,849,974; 4,168,284; 6,515,193; 6,323,157; 6,231,659; and 6,281,162. The disclosure of each of these U.S. patents is incorporated herein by reference. Effluent from oligomerization reactor 51 is passed into a second separator 59 wherein the effluent is separated into an oligomerized olefin stream (also referred to herein as a "heavy branched olefin stream") and a lighter fraction which contains C₉-C₁₃ olefins and /or C₁₄-C₁₈ paraffins (referred to herein as a "non-oligomerized olefin/paraffin stream"). The heavy branched olefins stream is combined with the hydrodewaxer product from hydrodewaxer 56 and routed to a hydrofinisher 57, or alternatively routed directly into hydrofinisher 57, where unsaturation is removed and appropriate thermal and oxidative stability is imparted to make the synthetic lubricant crude basestock. The synthetic lubricant crude basestock may then be distilled in distillation column 61 to recover a product-grade synthetic lubricant basestock fractions. Because some small amount of hydrocracking may occur in hydrofinisher 57, distillation column 61 acts to remove any light hydrocarbons, having a carbon number of less than about 15, and further removes any residual unsaturated hydrocarbons. In addition, distillation column 61 may be operated in a manner well known to those skilled in the art to obtain product fractions having specific viscosities, such as 2 cSt, 3 cSt, 4 cSt, 5 cSt, 6 cSt, and 7 cSt fractions.

[42] In yet another embodiment, the unreacted C₉-C₁₇ fraction, or a predominantly paraffinic C₁₄-C₁₈ fraction may be recovered as overhead from separator 59 and passed to dehydrogenation unit 58 wherein the stream is dehydrogenated over a dehydrogenation catalyst, such as platinum supported on a high-surface alumina with other metals potentially present to reduce undesirable reactions and coking. The reaction conditions are generally between about 800° and about 950°F, with hydrogen recycle equivalent to between about 4:1 and about 10:1 molar ratio of hydrogen to hydrocarbon, and sufficiently low pressure to keep the reactant in vapor phase. The dehydrogenation product can then be recycled through conduit 60 to the oligomerization reactor 51. Known dehydrogenation methods and conditions are disclosed in U.S. patents 6,498,280, 4,347,394; 6,414,209; 6,392,109; 6,187,981; 5,276,231; 3,681,442; and 3,910,994. The disclosure of each of these patents is incorporated herein by reference. Another known process of dehydrogenation useful in the process of the invention is that used in the PACOL™ process of UOP.

[43] In another embodiment of the process of the invention, all or part of LFTL is subjected to means for dehydrogenating hydrocarbons, particularly paraffins, to form olefins prior to oligomerization.

[44] The composition of the resulting baseoil product reflects the dual nature of branching in the product. The portion of the baseoil product processed through the hydrocracking/hydrodewaxing route contains solely methyl branches per molecule, while the portion made by oligomerization contains long-chain branching. The approximate ratio of methyl-branched species to the long-chain species may range from about 10:1 to about 1:1. In one particular embodiment, the ratio of methyl-branched to long chain species is about 8:1 on the average. The branching index, or BI, of the baseoils made from hydroisomerized Fischer-Tropsch wax having a pour point of -20°C is projected to be about 25%, while the BI of polyolefin - derived baseoil is about 21.8% on average. The average BI of the inventive baseoil is about 24.4% and may range from between about 23.4% and about 24.7%. The DM of the baseoils made from hydroisomerized Fischer-Tropsch wax is projected to be 21.4% for a fluid with -20°C pour point, while DM for a polyolefin is about 19.4% on average. The DM for the inventive baseoil ranges from between about 20.4% and about 21.2%. In one particular embodiment of the invention, the DM of the inventive lubricant basestock is about 21.1%.

[45] The inventive process is a relatively high yield process. First, alcohols are dehydrated so as to produce a homogeneous olefin/paraffin mixture which may be partially oligomerized to produce long-chain branched molecules. Thus, yield loss from alcohol content is eliminated or reduced with a concomitant increase in product yield. Second, hydrocracking and hydrodewaxing severity is decreased thereby producing a relatively high pour point material with relatively few solely methyl branches from the Fischer-Tropsch wax. When subsequently co-processed into a baseoil, these disparate molecular structures act to depress the pour point of the overall mixture, improve pour point depressant response and Brookfield viscosity while maintaining high thermal and oxidative stability.

[46] The process of the invention provides a synthetic lubricant crude basestock the viscosity profile of which may be customized, preferably shifted to production of more middle viscosity (from about 4 to about 6 cSt) or higher viscosity ($> 6\text{cSt}$) components. It is well known to those skilled in the art that the oligomerization reaction may be controlled so as to increase or decrease the molecular weight of the product oligomer, and thus the viscosity, of the oligomers produced by controlling the oligomerization reaction conditions, such as temperature, residence time, catalyst composition and conformation, catalyst amount, pressure, co-reactants, and additives. The methods of controlling the oligomerization reaction product by varying such parameters are well known to those skilled in the art, including those disclosed in U.S. 6,281,401; 5,243,112; 4,612,406; 4,254,295; 4,225,739; and 3,997,621, the disclosures of which are incorporated herein by reference. Moreover, the olefinic content and profile (alpha-olefins vs. internal olefins) of the feed to the oligomerization reactor may also be controlled by the process of the invention so as to tailor the resulting synthetic lubricant basestock viscosity profile. Fig. 6 compares the viscosity profile of a synthetic lubricant basestock produced by a typical Fischer-Tropsch synthesis (designated as "Hydroprocessed") with a synthetic lubricant basestock produced by the process of the invention (designated "HP + Oligomer"). As is apparent from Fig. 6, the basestock produced in accordance with the invention contains proportionately less lower viscosity component than typically produced Fischer-Tropsch lubricant basestock and proportionately more middle viscosity component than typical synthetic lubricant basestock.

[47] Embodiments of the invention provide numerous advantages over synthetic lubricant basestocks and processes for producing such basestocks of the prior art. Some of such advantages include:

- (1) conversion of lower carbon number Fischer-Tropsch products into high value end products thereby improving the economics of Fischer-Tropsch operations;
- (2) a synthetic lubricant basestock product having improved low temperature properties;
- (3) a synthetic lubricant basestock for which a product slate may be customized according to viscosity profile by regulation of the oligomerization reaction.

10 [48] What is claimed is: